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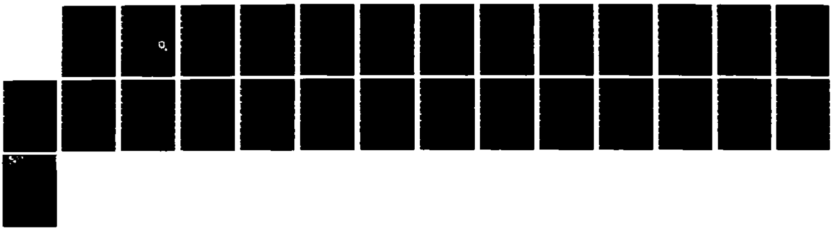

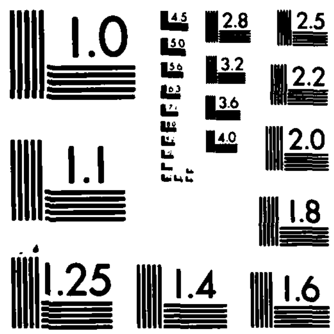

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Crystal-Field Splittings of the Hund Ground States of nd^N Ions in S_4 Symmetry: Theory and Application to the Ga^{3+} Site of $Gd_3Sc_2Ga_3O_{12}$

by Clyde A. Morrison
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U.S. Army Electronics Research
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B-sub nm - less than

A

A-sub nm

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We discuss the use of the weak-field approximation and the point-charge model to calculate the splittings of the Hund ground states of nd^N ions ($1 < N < 9$) in S_4 symmetry. The host crystal chosen as an illustration is $Gd_3Sc_2Ga_3O_{12}$ (gadolinium scandium gallium garnet—GSGG). In this crystal, the nd^N ions enter the Ga^{3+} sites substitutionally. Lattice sums, A_{nm}, are reported for the Ga^{3+} site, and crystal-field parameters, B_{nm}, and energy levels are given for 29 ions with N = 1 to 9. The results of the calculations are discussed for each ion considered.

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1. INTRODUCTION

The purpose of this report is to investigate the crystal-field splittings of the lowest level (the Hund ground state) of the configuration nd^N (n = 3, 4, 5 and $1 \leq N \leq 9$) in S_4 symmetry. The particular single-crystal material considered as an illustration of our methods is $Gd_3Sc_2Ga_3O_{12}$ (gadolinium scandium gallium garnet--GSGG), in which the Ga^{3+} ion site has S_4 symmetry. The material GSGG has recently[1,2] been shown to be an efficient laser host when doped substitutionally with Nd^{3+} (in the Gd site) and Cr^{3+} (in the Ga site). The high efficiency of this host crystal is due to broad-band absorption by chromium ions and to the efficient transfer of energy from Cr^{3+} ions to excited states of Nd^{3+} ions ($^4F_{3/2}$ and higher). The absorption bands of Cr^{3+} are much broader than those of Nd^{3+} so that more energy is extracted from the pump.

The theory presented here is an extension of previous work we have done on rare-earth ions.* The present calculations represent a zeroth-order approximation, in that effects of spin-orbit and related interactions are neglected entirely and the crystal field is assumed sufficiently weak so that it does not mix together different free-ion levels. (These two assumptions together constitute the so-called "weak-field approximation."[3-5]) Also, we use the simplest model to describe the host lattice, the point-charge model. Refinements of this model, such as dipole[6] and self-induced[7] contributions to the crystal field, considered elsewhere for rare-earth ions, are not included in this work.

---

[1]*E. V. Zharikov, N. N. Il'ichev, V. V. Laptev, A. A. Malyutin, V. G. Ostroumov, P. P. Pashinin, A. S. Pimenov, V. A. Smirnov, and I. A. Shcherbakov, Spectral, Luminescence, and Lasing Properties of Gadolinium Scandium Gallium Garnet Crystals Activated with Neodymium and Chromium Ions, Sov. J. Quantum Electron. 13 (1983), 82.*

[2]*B. Struve, G. Huber, V. V. Laptev, I. A. Shcherbakov, and E. V. Zharikov, Tunable Room-Temperature cw Laser Action in Cr^{3+}: GdScGa-Garnet, Appl. Phys. B30 (1983), 117.*

[3]*C. J. Ballhausen, Introduction to Ligand Field Theory, McGraw-Hill, New York (1962), chapter 4.*

[4]*J. S. Griffith, The Theory of Transition-Metal Ions, Cambridge Press, Cambridge, England (1961), chapter 8.*

[5]*D. S. McClure, Electronic Spectra of Molecules and Ions in Crystals, Part II. Spectra of Ions in Crystals, in Solid State Physics, Vol. 9, Academic Press, New York (1959), pp 399-525.*

[6]*C. A. Morrison, Dipolar Contributions to the Crystal Fields in Ionic Solids, Solid State Commun. 18 (1976), 153.*

[7]*C. A. Morrison, G. F. de Sá, and R. P. Leavitt, Self-Induced Multipole Contribution to the Single-Electron Crystal Field, J. Chem. Phys. 76 (1982), 3899.*

**The theory for rare-earth ions is discussed in a sequence of 14 technical reports of Harry Diamond Laboratories published between October 1973 and February 1977, entitled Rare Earth Ion-Host Interactions.*

2. THEORY

In the weak-field approximation, it is assumed that the mutual Coulomb interactions among the d^N electrons in the free ion are much larger than the same interaction of these electrons with the crystalline field. Also, both the Coulomb interaction and the interaction with the crystal field are assumed much larger than the spin-orbit interaction. Thus, in the remainder of the discussion, we shall ignore the spin-orbit interaction. For the $3d^N$ series, these assumptions are quite good, but they become less valid[5] for n = 4 or 5.

The Coulomb interaction within the nd^N configuration can be written as[8]

$$H_c = \frac{1}{2} \sum_{i \neq j}^{N} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} ,$$

or

$$H_c = \sum_k \sum_{i \neq j}^{N} F^{(k)} C^*_{kq}(r_i) C_{kq}(\hat{r}_j) , \tag{1}$$

where the $F^{(k)}$ (Slater parameters) are given by

$$F^{(k)} = 2e^2 \int_0^\infty R^2_{nd}(r)\, dr \int_r^\infty R^2_{nd}(r') \frac{r^k}{r'^{k+1}}\, dr' . \tag{2}$$

For d electrons only terms in equation (1) with $k \leq 4$ have nonvanishing matrix elements, and thus only $F^{(2)}$ and $F^{(4)}$ are needed. The $C_{kq}(r)$ are unnormalized spherical tensors related to the more familiar spherical harmonics $Y_{kq}(r)$ by

$$C_{kq}(\hat{r}) = \sqrt{\frac{4\pi}{2k+1}}\, Y_{kq}(\hat{r}) .$$

The matrix elements of the Coulomb interaction are given by Nielson and Koster[9] in the form

$$\langle \alpha' L' S' | H_c | \alpha L S \rangle = \delta_{LL'} \delta_{SS'} \sum_k c_k(\alpha', \alpha, L, S) F^{(k)} ; \tag{3}$$

the coefficients $c_k(\alpha', \alpha, L, S)$ are tabulated elsewhere[9] for each of the states of d^N for $1 \leq N \leq 5$. For N > 5 the matrix elements of d^{10-N} are identical to those of d^N.

[5] *D. S. McClure, Electronic Spectra of Molecules and Ions in Crystals, Part II. Spectra of Ions in Crystals, in Solid State Physics, Vol. 9, Academic Press, New York (1959), pp 399-525.*

[8] *B. R. Judd, Operator Techniques in Atomic Spectroscopy, McGraw-Hill, New York (1963), p 221.*

[9] *C. W. Nielson and G. F. Koster, Spectroscopic Coefficients for the p^n, d^n and f^n Configurations, The MIT Press, Cambridge, MA (1963), p 53.*

Eigenstates of the Coulomb interaction are found by diagonalizing the matrix formed by equation (3) for a given L and S. For states of maximum multiplicity, there is only one state for a given L and S; in particular, the Hund ground states have S as the maximum possible value (= N/2 for N $\leq$ 5) and L the maximum value consistent with S (= N(7 - N)/2 for N $\leq$ 5). Thus the Hund ground states are ^2D, ^3F, ^4F, ^5D, and ^6S for d^1, d^2, d^3, d^4, and d^5, respectively. For N > 5, Hund ground states of d^N are the same as those for d^{10-N}. The Slater parameters are obtained either by being fit to experimental data or by being calculated using Hartree-Fock wave functions.[10] In general, the Hartree-Fock $F^{(k)}$ are much larger than the corresponding $F^{(k)}$ obtained by fitting to the experimental data on free ions. Further, the $F^{(k)}$ for ions in crystals are reduced compared with their free-ion values.*

The interaction of the d^N electrons with the crystal field is taken as[10]

$$H_{CEF} = \sum_{nm} B^*_{nm} \sum_i C_{nm}(r_i) \quad , \tag{4}$$

where, for d electrons, n = 2 and 4 only, and where the allowed values of m depend on the crystal symmetry. The crystal-field interaction given in equation (4) can be written in terms of Racah's unit tensors[11] as

$$H_{CEF} = \sqrt{\frac{10}{7}} \sum_n (-1)^{n/2} B^*_{nm} U^{(n)}_m \quad . \tag{5}$$

The matrix elements of the unit tensors, $U^{(n)}_m$, in equation (5) can be calculated using the Wigner-Eckart theorem to give

$$\langle \alpha' L' M'_L S' M'_S | U^{(n)}_m | L M_L S M_S \rangle = \frac{\langle L(M_L) n(m) | L'(M'_L) \rangle}{\sqrt{2L' + 1}} \left(\alpha' L' S \middle|\middle|^{(n)}\middle|\middle| \alpha L S\right) \delta_{SS'} \delta_{M_S M'_S} \quad , \tag{6}$$

where the reduced matrix elements, $\left(\alpha' L' S \middle|\middle| U^{(n)} \middle|\middle| \alpha L S\right)$, are tabulated (with no additional factors) elsewhere.[9] The quantity in angular brackets in equation (6) is a Clebsch-Gordan coefficient (proportional to a 3-j symbol) and is

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[9]*C. W. Nielson and G. F. Koster, Spectroscopic Coefficients for the p^n, d^n and f^n Configurations, The MIT Press, Cambridge, MA (1963), p 53.*

[10]*B. G. Wybourne, Spectroscopic Properties of Rare Earths, Interscience Publishers, New York (1965).*

[11]*G. Racah, Theory of Complex Spectra I-IV, Phys. Rev. 61 (1942), 186; Phys. Rev. 62 (1942), 438; Phys. Rev. 63 (1942), 367; Phys. Rev. 76 (1949), 1352.*

**The theory for rare-earth ions is discussed in a sequence of 14 technical reports of Harry Diamond Laboratories published between October 1973 and February 1977, entitled Rare Earth Ion-Host Interactions.*

tabulated.[12] Thus the calculation of the crystal-field splittings can be performed once the crystal-field parameters, B_{nm}, are known.

In the point-charge model* of the crystal field, the parameters B_{nm} are given by

$$B_{nm} = \langle r^n \rangle A_{nm} \qquad (7)$$

where $\langle r^n \rangle$ is the radial expectation value of r^n calculated using Hartree-Fock wave functions, and the A_{nm} are the coefficients of a multipolar expansion of the crystal field at the site occupied by the the transition-metal ion. The A_{nm} have been evaluated for the S_4 and D_{2d} sites (equivalent for the d^N configuration) in a number of solids.[13]

Frequently in the analysis of the spectra of a transition-metal ion in a solid, a cubic-field approximation is made; however, there seems to be no consistent method of making this approximation. For example, suppose the ion were in S_4 symmetry; then the nonvanishing crystal-field parameters are B_{20}, B_{40}, and B_{44}. In any cubic approximation, B_{20} is assumed to be zero. The question is how to select the best cubic B^c_{nm} from the B_{40} and B_{44} corresponding to S_4 symmetry. Recently,[14] the role of the rotational invariants given by

$$\overline{S}_n = \left[\frac{1}{2n+1} \sum_{nm} B^*_{nm} B_{nm}\right]^{1/2} \qquad (8)$$

has been discussed. The $\overline{S}_n$ have the the property of invariance under arbitrary coordinate rotation. The choice of B^c_{40} can be made unique by requiring that the corresponding $\overline{S}_4$ parameters in S_4 and cubic symmetries be equal. We have

$$B^c_{40} = \lambda B_{40} \quad , \qquad (9)$$

where

$$\lambda = \left[7\left(1 + 2B^2_{44}/B^2_{40}\right)/12\right]^{1/2} \quad , \qquad (10)$$

where we have used the relation $B^c_{44} = 5B^c_{40}/\sqrt{70}$ as required in the cubic groups.

---

[12] *M. Rotenberg, R. Bivins, N. Metropolis, and J. Wooten, Jr., The 3-j and 6-j Symbols, Technology Press, Massachusetts Institute of Technology, Cambridge, MA (1959).*

[13] *N. Karayianis and C. A. Morrison, Rare Earth Ion-Host Interactions: 1. Point Charge Lattice Sum in Scheelites, Harry Diamond Laboratories, HDL-TR-1648 (October 1973).*

[14] *R. P. Leavitt, On the Role of Certain Rotational Invariants in Crystal-Field Theory, J. Chem. Phys. 77 (1982), 1661.*

**The theory for rare-earth ions is discussed in a sequence of 14 technical reports of Harry Diamond Laboratories published between October 1973 and February 1977, entitled Rare Earth Ion-Host Interactions.*

3. LATTICE SUMS FOR $Gd_3Sc_2Ga_3O_{12}$

The crystallographic and x-ray data[15] on GSGG are given in table 1. Also contained in the table are the ionic radii[16] and the effective charges of the constituent ions. Six oxygen ions surround the Sc^{3+} ion at a distance of 2.04 Å,* and four oxygen ions surround the Ga^{3+} ion at a distance of 1.89 Å. (From the ionic radii we obtain 2.13 Å and 1.87 Å, respectively.) When the crystal is doped with an ion, it is important that the ionic radius of the dopant ion nearly match the ionic radius of the constituent ion it is to replace. The point-charge contributions to the A_{nm} were calculated† using the data given in table 1; the results are A_{20} = 739 $cm^{-1}/Å^2$, A_{40} = -13,749 $cm^{-1}/Å^4$, and A_{44} = 5,515 $cm^{-1}/Å^4$. (The coordinate system has been rotated so that A_{44} is real and positive.)

TABLE 1. CRYSTALLOGRAPHIC AND X-RAY DATA,[a] IONIC RADII,[b] AND EFFECTIVE CHARGES FOR $Gd_3Sc_2Ga_3O_{12}$

Ion	Site[c]	Cubic space group Ia3d, No. 230, Z = 8				i.r.[d] (Å)	q(e)
		Symmetry	x	y	z		
Gd	24(c)	D_2	0	1/4	1/8	1.06	3
Sc	16(a)	C_{3i}	0	0	0	0.73	3
Ga	24(d)	S_4	3/8	0	1/4	0.47	3
O[e]	96(h)	C_1	-0.0202	0.0558	0.1501	1.40	-2

[a]*C. D. Brandle and R. L. Barns, Crystal Stoichiometry and Growth of Rare-Earth Garnets Containing Scandium, J. Cryst. Growth 20 (1979), 1.*

[b]*R. D. Shannon and C. T. Prewitt, Effective Ionic Radii in Oxides and Fluorides, Acta Crystallogr. B25 (1969), 925; Acta Crystallogr. B26 (1970), 1046.*

[c]*For a description of the notation, see N. F. M. Henry and K. Lonsdale, eds., International Tables for X-Ray Crystallography, vol. I. Symmetry Groups, Kynoch, Birmingham, England (1969).*

[d]*i.r. = ionic radius.*

[e]*Coordinates of oxygen ion are from C. A. Morrison and R. P. Leavitt, Spectroscopic Properties of Triply Ionized Lanthanides in Transparent Host Materials, in Handbook on the Physics and Chemistry of Rare Earths, vol. 5, ed. by K. A. Gschneidner and L. Eyring, Jr., North-Holland, New York (1982), p 643.*

4. THE d^1 AND d^9 CONFIGURATIONS

Table 2 gives the values, where known, of $\langle r^2 \rangle$, $\langle r^4 \rangle$, ionic radii (i.r.), and energy of the next configuration above the ground configuration relative to the ground state (Δ) for a number of ions with the configurations nd^1 and

[15]*C. D. Brandle and R. L. Barns, Crystal Stoichiometry and Growth of Rare-Earth Garnets Containing Scandium, J. Cryst. Growth 20 (1979), 1.*

[16]*R. D. Shannon and C. T. Prewitt, Effective Ionic Radii in Oxides and Fluorides, Acta Crystallogr. B25 (1969), 925; Acta Crystallogr. B26 (1970), 1046.*

**10 Å = 1 nm.*

†*C. A. Morrison, R. P. Leavitt, and M. D. Gildner, Rare Earth Ion-Host Lattice Interactions: 15. Analysis of the Spectra of Nd^{3+} in $Gd_3Sc_2Ga_3O_{12}$, HDL Technical Report (in press).*

nd^9. The ions given in table 2 were chosen because data exist on them concerning crystal growth, optical spectra, or electron spin resonance. Unfortunately, Fraga et al[17] do not calculate values of $\langle r^k \rangle$ for ionization states greater than 3 for the nd^N ions. Thus, we cannot complete the crystal-field calculations on these highly ionized ions.

TABLE 2. DATA ON IONS WITH nd^1 AND nd^9 CONFIGURATIONS[a]

Ion	Configuration	$\langle r^2 \rangle$ ($Å^2$)	$\langle r^4 \rangle$ ($Å^4$)	i.r.[b] (Å)	Δ (cm^{-1})
Ti^{3+}	$3d^1$	0.5341	0.5769	0.67	80,389[c]
V^{4+}	$3d^1$	---	---	0.59	148,143[d]
Cu^{2+}	$3d^9$	0.2489	0.2097	0.62[e]	12,600[f]
Zn^{3+}	$3d^9$	0.2297	0.1200	---	---
Nb^{4+}	$4d^1$	---	---	0.69	74,000[f]
Mo^{5+}	$4d^1$	---	---	0.63	118,000[f]
Pd^{1+}	$4d^9$	0.6899	0.9612	0.59[g]	31,500[f]
Ag^{2+}	$4d^9$	0.5516	0.5644	0.89	63,000[f]
Ta^{4+}	$5d^1$	---	---	0.66	---

[a]*Values of $\langle r^n \rangle$ are from reference 17 and ionic radii are from reference 16. The quantity Δ is the energy of the next configuration above the ground configuration relative to the ground state.*

[b]*i.r. = ionic radius.*

[c]*C. Corliss and J. Sugar, Energy Levels of Titanium, TiI through TiXXII, J. Phys. Chem. Ref. Data 8 (1979), 1.*

[d]*J. Sugar and C. Corliss, Energy Levels of Vanadium, VI through VXXIII, J. Phys. Chem. Ref. Data 7 (1978), 1191.*

[e]*For 4 coordination.*

[f]*C. E. Moore, Atomic Energy Levels as Derived from the Analysis of Optical Spectra, volumes I, II, and III, National Bureau of Standards (1971).*

[g]*For 2 coordination.*

The matrix elements of the crystal field were computed using equation (7); the results are given in table 3. The notation for the irreducible representations (IR) of S_4 is that of Koster et al.[18] Since in the S_4 group the energy levels for Γ_3 and Γ_4 are degenerate, the matrix elements for Γ_3 are omitted. Using the results from table 2, we calculated the crystal-field parameters, B_{nm}, for the Ga^{3+} site in GSGG. These results are given in table 4 along with the cubic B_{40}^C obtained from equation (10). The energy levels of d^1 and d^9 ions were computed using the data in tables 3 and 4, and the results are given in table 5. Note that levels of d^9 are inverted relative to levels of d^1. The results for Ti^{3+} indicate that unless the crystal field is severely underestimated and the next electronic configuration is lowered

[9]*C. W. Nielson and G. F. Koster, Spectroscopic Coefficients for the p^n, d^n and f^n Configurations, The MIT Press, Cambridge, MA (1963), p 53.*

[17]*S. Fraga, J. Karwowski, and K. M. S. Saxena, Physical Sciences Data, Vol. 5, Handbook of Atomic Data, Elsevier/North-Holland, New York (1976). [The values of $\langle r^k \rangle$ are not reported for ionization states greater than 3.]*

[18]*G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, Properties of the Thirty-Two Point Groups, MIT Press, Cambridge, MA (1963).*

considerably, only the far-infrared spectrum of this ion would be observed. The relatively small splittings of the Zn^{3+} ion and the relatively large value for ζ, the spin-orbit parameter,[17] indicate that more accurate levels for this ion would be obtained by diagonalizing simultaneously the crystal-field and spin-orbit interactions within the ^2D state.

TABLE 3. MATRIX ELEMENTS IN S_4 SYMMETRY OF CRYSTAL FIELD FOR ^2D STATE OF nd^1 AND ^5D STATE OF nd^6

Note: For the corresponding matrix elements for the ^2D state of nd^9 and the ^5D state of nd^4, multiply all entries by -1.[a]

M'	M	IR[b]	B_{20}	B_{40}	B_{44}
0	0	Γ_1	2/7	2/7	0
-2	-2	Γ_2	-2/7	1/21	0
-2	2	Γ_2	0	0	$\sqrt{70}/21$
2	2	Γ_2	-2/7	1/21	0
-1	-1	Γ_4	1/7	-4/21	0

[a]*The matrix elements of Γ_3 are not given, as they are equal to those for Γ_4.*
[b]*IR = irreducible representation.*

TABLE 4. CRYSTAL-FIELD PARAMETERS, B_{nm} (cm^{-1}), FOR nd^1 AND nd^9 IONS IN Ga^{3+} SITE IN GSGG

Ion	B_{20}	B_{40}	B_{44}	B^c_{40}
Ti^{3+}	394.7	-7,932	3,182	-6,965
Cu^{2+}	184.0	-2,883	1,156	-2,531
Zn^{3+}	169.8	-1,649	661.6	-1,448
Pd^{1+}	509.9	-13,215	5,301	-11,604
Ag^{2+}	407.6	-7,759	3,112	-6,813

TABLE 5. ENERGY LEVELS (cm^{-1}) FOR ^2D LEVEL OF nd^1 AND nd^9 IONS IN Ga^{3+} SITE OF GSGG

IR[a]	Γ_1	Γ_2	Γ_2	$\Gamma_{3,4}$
Ti^{3+}	0	395	2,930	3,720
Cu^{2+}	1,346	1,225	304	0
Zn^{3+}	761	729	201	0
Pd^{1+}	6,220	5,476	1,253	0
Ag^{2+}	3,636	3,262	732	0

[a]*IR = irreducible representation.*

[17]*S. Fraga, J. Karwowski, and K. M. S. Saxena, Physical Sciences Data, Vol. 5, Handbook of Atomic Data, Elsevier/North-Holland, New York (1976). [The values of $\langle r^k \rangle$ are not reported for ionization states greater than 3.]*

5. THE d^2 AND d^8 CONFIGURATIONS

The Hund ground state for nd^2 is ^3F. The ions with d^2 and d^8 configurations selected for investigation in the Ga^{3+} site in GSGG are given in table 6. The ionic radii of the ions given in table 6 are for coordination number 6 and are considerably larger than the i.r. for Ga^{3+} in 4 coordination. However, if say V^{3+} could be substituted into the 4 coordination site, the i.r. would be considerably reduced (the i.r. for Ga^{3+} is 0.47 Å for 4 coordination and 0.620 Å for 6 coordination[16]). Of the ions with the d^8 configuration, it would appear that Ni^{2+} has the best chance of replacing Ga^{3+} in GSGG. The matrix elements of the crystal-field interaction for the ^3F state of nd^2 are given in table 7. The largest matrix is 2 × 2, which occurs for the Γ_2 and the $\Gamma_{3,4}$ doublets. The crystal-field parameters for the Ga^{3+} site in GSGG given in table 8 were computed using the results of tables 6 and 7. The crystal-field parameters were used to compute the energy levels of the 10 ions given in table 6; the results are given in table 9 (p 14). For the V^{3+} ion, the total crystal-field splitting is small (4,600 cm^{-1}) compared to the free-ion splitting (16,700 cm^{-1}), so that the influence of the next configuration, ^3P, can be ignored in a first approximation. However for Ti^{2+} the free-ion energy separation ^3F-^3P and the crystal-field splittings are the same order of magnitude, so that a more precise crystal-field calculation must include the ^3P state. In the case of Nb^{3+}, the crystal-field splitting is much larger than the free-ion energy spacing of the ^3F-^3P levels, which

TABLE 6. DATA ON IONS WITH nd^2 AND nd^8 CONFIGURATIONS[a]

Ion	Configuration	$\langle r^2 \rangle$ ($Å^2$)	$\langle r^4 \rangle$ ($Å^4$)	i.r.[b] (Å)	Δ (cm^{-1})
Ti^{2+}	$3d^2$	0.6716	0.9808	0.86	10,419[c]
V^{3+}	$3d^2$	0.4571	0.4270	0.64	16,700[d]
Ni^{2+}	$3d^8$	0.3203	0.2478	0.69	8,500[e]
Nb^{3+}	$4d^2$	0.9282	1.4606	0.70	9,000[e]
Rh^{1+}	$4d^8$	0.7682	1.1872	---	9,000[e]
Pd^{2+}	$4d^8$	0.6045	0.6744	0.64[f]	10,600[e]
Ag^{3+}	$4d^8$	0.4993	0.4372	0.65[f]	---
Ta^{3+}	$5d^2$	1.0416	1.7777	0.67	---
Pt^{2+}	$5d^8$	0.7474	0.9649	0.60[f]	---
Au^{3+}	$5d^8$	0.6357	0.6646	0.70[f]	---

[a]*Values of $\langle r^n \rangle$ and ionic radius are from references 17 and 16, respectively. The quantity Δ is the difference in energy between ^3P and ^3F states in the free ion.*
[b]*i.r. = ionic radius.*
[c]*C. Corliss and J. Sugar, Energy Levels of Titanium, TiI through TiXXII, J. Phys. Chem. Ref. Data 8 (1979), 1.*
[d]*J. Sugar and C. Corliss, Energy Levels of Vanadium, VI through VXXIII, J. Phys. Chem. Ref. Data 7 (1978), 1191.*
[e]*C. E. Moore, Atomic Energy Levels as Derived from the Analysis of Optical Spectra, volumes I, II, and III, National Bureau of Standards (1971).*
[f]*For 4 coordination.*

[16]*R. D. Shannon and C. T. Prewitt, Effective Ionic Radii in Oxides and Fluorides, Acta Crystallogr. B25 (1969), 925; Acta Crystallogr. B26 (1970), 1046.*

indicates that even for a first estimate of the splittings, both the ^3F and ^3P levels should be included. Because of the large values of ζ for the d^8 ions,[17] the approximations used in the calculations for these ions are probably poor, the only exception being perhaps Ni^{2+}.

TABLE 7. MATRIX ELEMENTS IN S_4 SYMMETRY OF CRYSTAL FIELD FOR ^3F STATE OF nd^2

Note: For the corresponding matrix elements for the ^3F state of nd^8, multiply all entries by -1.[a]

M'	M	IR[b]	B_{20}	B_{40}	B_{44}
0	0	Γ_1	4/35	-2/7	0
-2	-2	Γ_2	0	1/3	0
-2	2	Γ_2	0	0	$-\sqrt{70}/21$
2	2	Γ_2	0	1/3	0
-1	-1	Γ_4	3/35	-1/21	0
-1	3	Γ_4	0	0	$-\sqrt{42}/21$
3	3	Γ_4	-1/7	-1/7	0

[a]*The matrix elements of Γ_3 are not given, as they are equal to those for Γ_4.*
[b]*IR = irreducible representation.*

TABLE 8. CRYSTAL-FIELD PARAMETERS, B_{nm} (cm^{-1}), FOR nd^2 and nd^8 IONS IN Ga^{3+} SITE IN GSGG

Ion	B_{20}	B_{40}	B_{44}	B^c_{40}
Ti^{2+}	496.3	-13,485	5,409	-11,800
V^{3+}	337.8	-5,870	2,355	-5,155
Ni^{2+}	236.7	-3,407	1,367	-2,992
Nb^{3+}	685.9	-20,082	8,055	-17,634
Rh^{1+}	567.7	-16,323	6,548	-14,334
Pd^{2+}	446.7	-9,272	3,719	-8,142
Ag^{3+}	369.0	-6,011	2,411	-5,278
Ta^{3+}	769.8	-24,442	9,804	-21,462
Pt^{2+}	552.3	-13,267	5,322	-11,650
Au^{3+}	469.7	-9,138	3,665	-8,024

6. THE d^3 AND d^7 CONFIGURATIONS

A number of ions with nd^3 or nd^7 configurations are listed in table 10 along with the $\langle r^k \rangle$, i.r., and Δ values. Most of these ions could have small enough i.r. in 4 coordination to fit in the Ga^{3+} site if methods could be found to properly dope the crystal. Because of the relative importance of Cr^{3+} in GSGG, we have included the matrix elements of the crystal field in both ^4F and ^4P states in table 11. The calculations reported here only involve the ^4F part of the crystal-field matrix, but further work will employ all the matrix elements given in table 11.

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[17]*S. Fraga, J. Karwowski, and K. M. S. Saxena, Physical Sciences Data, Vol. 5, Handbook of Atomic Data, Elsevier/North-Holland, New York (1976). [The values of $\langle r^k \rangle$ are not reported for ionization states greater than 3.]*

TABLE 9. ENERGY LEVELS (cm^{-1}) FOR ^3F LEVEL OF nd^2 AND nd^8 IONS IN Ga^{3+} SITE OF GSGG

IR[a]	Γ_2	Γ_2	$\Gamma_{3,4}$	$\Gamma_{3,4}$	Γ_1
Ti^{2+}	0	4,310	6,151	9,688	10,559
V^{3+}	0	1,876	2,678	4,209	4,610
Ni^{2+}	2,680	1,591	1,125	239	0
Nb^{3+}	0	6,418	9,159	14,432	15,719
Rh^{1+}	12,778	7,561	5,332	1,047	0
Pd^{2+}	7,272	4,308	3,042	617	0
Ag^{3+}	4,723	2,802	1,980	414	0
Ta^{3+}	0	7,812	11,147	17,570	19,124
Pt^{2+}	10,396	6,155	4,343	867	0
Au^{3+}	7,170	4,250	3,001	613	0

[a]*IR = irreducible representation.*

TABLE 10. DATA ON IONS WITH nd^3 AND nd^7 CONFIGURATIONS[a]

Ion	Configuration	$\langle r^2 \rangle$ (Å^2)	$\langle r^4 \rangle$ (Å^4)	i.r.[b] (Å)	Δ (cm^{-1})
V^{2+}	$3d^3$	0.5677	0.7112	0.79	12,600[c]
Cr^{3+}	$3d^3$	0.4018	0.3344	0.615	17,400[d]
Co^{2+}	$3d^7$	0.3525	0.2949	0.65	~14,000[e]
Ni^{3+}	$3d^7$	0.2705	0.1615	0.56	~16,000[f]
Nb^{2+}	$4d^3$	1.0769	2.0761	0.71	24,800[c,g]
Mo^{3+}	$4d^3$	0.9288	1.1461	0.67	60,000[c,g]
Pd^{3+}	$4d^7$	0.5435	0.5147	0.76	---
W^{3+}	$5d^3$	0.9400	1.4438	---	---

[a]*Values of $\langle r^n \rangle$ and ionic radius are from references 17 and 16, respectively. The quantity Δ is the difference in energy between ^4P and ^4F states in the free ion.*

[b]*i.r. = ionic radius.*

[c]*J. Sugar and C. Corliss, Energy Levels of Vanadium, VI through VXXIII, J. Phys. Chem. Ref. Data 7 (1978), 1191.*

[d]*J. Sugar and C. Corliss, Energy Levels of Chromium, CrI through CrXXIV, J. Phys. Chem. Ref. Data 6 (1977), 317.*

[e]*J. Sugar and C. Corliss, Energy Levels of Cobalt, CoI through CoXXVII, J. Phys. Chem. Ref. Data 10 (1981), 1097.*

[f]*C. Corliss and J. Sugar, Energy Levels of Nickel, NiI through NiXXVIII, J. Phys. Chem. Ref. Data 10 (1981), 197.*

[g]*Δ is the difference in energy between $(4d^25s)^4F$ and $(4d^3)^4F$ in the free ion.*

Table 12 gives the crystal-field parameters computed from the results given in tables 10 and 11. Of the ions with the nd^3 configuration, the largest crystal-field parameters are for Nb^{2+}; from the results given in table 13 (p 16) it would appear that all the matrix elements given in table 11 should be used in the calculation. However, it does not appear that using the full matrix will appreciably affect the levels of Cr^{3+}, since the crystal-field splitting is only 3,614 cm^{-1} and the ^4F-^4P levels are split by 17,400 cm^{-1}. For both Ni^{3+} and Co^{2+}, the approximations used in the calculations are reasonable. However, the value of ζ for Pd^{3+} and the proximity of several excited states indicate that a reasonable calculation for this ion would include several states of $4d^7$.

TABLE 11. MATRIX ELEMENTS, IN S_4 SYMMETRY, OF CRYSTAL FIELD FOR ^4F AND ^4P STATES OF nd^3

Note: For the corresponding matrix elements for ^4F and ^4P states of nd^7, multiply all entries by -1.[a]

L'M'	L M	IR[b]	B_{20}	B_{40}	B_{44}
3 0	3 0	Γ_1	-4/35	2/7	0
3 0	1 0	Γ_1	12/35	-4/21	0
1 0	1 0	Γ_1	2/5	0	0
3-2	3-2	Γ_2	0	-1/3	0
3-2	3 2	Γ_2	0	0	$\sqrt{70}/21$
3 2	3 2	Γ_2	0	-1/3	0
3-1	3-1	Γ_4	-3/35	1/21	0
3-1	3 3	Γ_4	0	0	$\sqrt{42}/21$
3-1	1-1	Γ_4	$2\sqrt{6}/35$	$\sqrt{6}/21$	0
3 3	3 3	Γ_4	1/7	1/7	0
3 3	1-1	Γ_4	0	0	$2\sqrt{7}/21$
1-1	1-1	Γ_4	-1/5	0	0

[a]*The matrix elements of Γ_3 are not given, as they are equal to those for Γ_4. Before the matrix is diagonalized, the Coulomb energies from equation (3) for the ^4F and ^4P states should be added to the diagonal elements.*

[b]*IR = irreducible representation.*

TABLE 12. *CRYSTAL-FIELD PARAMETERS, B_{nm} (cm^{-1}),* FOR nd^3 AND nd^7 IONS IN Ga^{3+} SITE IN GSGG

Ion	B_{20}	B_{40}	B_{44}	B^c_{40}
V^{2+}	419.5	-9,778	3,922	-8,586
Cr^{3+}	296.9	-4,597	1,844	-4,037
Co^{2+}	260.5	-4,054	1,626	-3,560
Ni^{3+}	199.9	-2,221	890.8	-1,950
Nb^{2+}	795.8	-28,545	11,450	-25,065
Mo^{3+}	686.4	-15,757	6,320	-13,836
Pd^{3+}	401.6	-7,077	2,839	-6,214
W^{3+}	694.6	-19,851	7,963	-17,431

7. THE d^4 AND d^6 CONFIGURATIONS

Of the ions with the nd^4 and nd^6 configurations listed in table 14, it would seem likely that Mn^{3+}, Rh^{3+}, or Ir^{3+} could be substituted for Ga^{3+} in GSGG. Unfortunately, the [illegible] ions Os^{4+} and Ru^{4+} with quite small i.r. (which might possibly enter the Ga^{3+} site) do not have reported values for $\langle r^k \rangle$. The matrix elements for the ^5D state of the nd^4 and nd^6 configurations are given in table 3. The crystal-field parameters given in table 15 were used to

TABLE 13. ENERGY LEVELS (cm^{-1}) FOR ^4F LEVEL OF nd^3 AND nd^7 IONS IN Ga^{3+} SITE OF GSGG

IR[a]	Γ_1	$\Gamma_{3,4}$	$\Gamma_{3,4}$	Γ_2	Γ_2
V^{2+}	0	641	3,202	4,538	7,663
Cr^{3+}	0	319	1,516	2,145	3,614
Co^{2+}	3,187	2,905	1,850	1,295	0
Ni^{3+}	1,752	1,588	1,013	709	0
Nb^{2+}	0	1,796	9,305	13,199	22,323
Mo^{3+}	0	1,036	5,162	7,314	12,351
Pd^{3+}	5,557	5,075	3,229	2,261	0
W^{3+}	0	1,274	6,485	9,195	15,540

[a]*IR = irreducible representation.*

TABLE 14. DATA ON IONS WITH nd^4 AND nd^6 CONFIGURATIONS[a]

Ion	Configuration	$\langle r^2 \rangle$ ($Å^2$)	$\langle r^4 \rangle$ ($Å^4$)	i.r.[b] (Å)	Δ (cm^{-1})
Cr^{2+}	$3d^4$	0.4910	0.5401	0.73	13,900[c]
Mn^{3+}	$3d^4$	0.3578	0.2688	0.58	21,000[d]
Fe^{2+}	$3d^6$	0.3893	0.3527	0.63[e]	19,160[f]
Co^{3+}	$3d^6$	0.2947	0.1884	0.525	14,560[g]
Ru^{4+}	$4d^4$	---	---	0.620	---
Rh^{3+}	$4d^6$	0.5936	0.6094	0.665	---
Pd^{4+}	$4d^6$	---	---	0.62	---
Os^{4+}	$5d^4$	---	---	0.630	---
Ir^{3+}	$5d^6$	0.7309	0.8745	0.73	---
Pt^{4+}	$5d^6$	---	---	0.63	---

[a]*Values of $\langle r^n \rangle$ and ionic radius are from references 17 and 16, respectively. The quantity Δ is the difference in energy between ^3H and ^5D states in the free ion.*

[b]*i.r. = ionic radius.*

[c]*J. Sugar and C. Corliss, Energy Levels of Chromium, CrI through CrXXIV, J. Phys. Chem. Ref. Data 6 (1977), 317.*

[d]*C. Corliss and J. Sugar, Energy Levels of Manganese, MnI through MnXXV, J. Phys. Chem. Ref. Data 6 (1977), 1253.*

[e]*For 4 coordination.*

[f]*C. Corliss and J. Sugar, Energy Levels of Iron, FeI through FeXXVI, J. Phys. Chem. Ref. Data 11 (1982), 135.*

[g]*J. Sugar and C. Corliss, Energy Levels of Cobalt, CoI through CoXXVII, J. Phys. Chem. Ref. Data 10 (1981), 1097.*

calculate the results given in table 16. For Mn^{3+}, Fe^{2+}, and Co^{3+}, the crystal-field splittings are small compared to the spacing to the next free-ion level, so that ignoring the effects of these higher levels seems justified. However, the crystal-field splitting for Cr^{2+} is appreciable when compared to the ^5D-^3H separation given in table 14; thus, higher levels might have to be considered. Since the ground state has spin two and the next higher states have spin zero, the spin-orbit interaction must be considered in the calculation. The spin-orbit coupling constant, ζ, is quite small for both Mn^{3+} and Cr^{2+} but is quite large for Ru^{4+}, Os^{4+}, Ir^{3+}, and Rh^{3+}. In any serious investigation of these latter four ions, the spin-orbit interaction should be taken into consideration.

TABLE 15. CRYSTAL-FIELD PARAMETERS, B_{nm} (cm^{-1}), FOR nd^4 AND nd^6 IONS IN Ga^{3+} SITE IN GSGG

Ion	B_{20}	B_{40}	B_{44}	B_{40}^{c}
Cr^{2+}	362.8	-7,426	2,979	-6,521
Mn^{3+}	264.4	-3,695	1,482	-3,245
Fe^{2+}	287.7	-4,850	1,945	-4,258
Co^{3+}	217.8	-2,591	1,039	-2,275
Rh^{3+}	438.7	-8,379	3,361	-7,358
Ir^{3+}	540.1	-12,024	4,823	-10,558

TABLE 16. ENERGY LEVELS (cm^{-1}) FOR ^5D LEVEL OF nd^4 AND nd^6 IONS IN Ga^{3+} SITE OF GSGG

IR[a]	$\Gamma_{3,4}$	Γ_2	Γ_2	Γ_1
Cr^{2+}	0	736	3,110	3,484
Mn^{3+}	0	402	1,583	1,721
Fe^{2+}	2,268	1,765	215	0
Co^{3+}	1,202	906	78	0
Rh^{3+}	3,927	3,083	405	0
Ir^{3+}	5,648	4,475	632	0

[a] *IR = irreducible representation.*

8. THE d^5 CONFIGURATION

The values of $\langle r^k \rangle$, i.r., and Δ for five ions with the nd^5 configuration are given in table 17. Of these ions it seems quite likely that Fe^{3+} could be doped into the Ga^{3+} site in GSGG very easily. The crystal-field parameters for three of the ions listed in table 17 have been calculated using the results given there and in section 3. These crystal-field parameters are listed in table 18. Unfortunately, the ground state of the nd^5 configuration is an S state and does not split in a crystal field unless the spin-orbit interaction is taken into consideration. The inclusion of the spin-orbit interaction mixes the states with spin 3/2, particularly the ^4P state, into the ground state with spin 5/2. The ^4P state would be coupled by the crystal field to a number of states with spin 3/2 (^4G, etc). These latter states are quite closely spaced in the free ion; consequently they all need to be taken into consideration in a realistic calculation. This procedure would lead to large matrices which would include the crystal-field, spin-orbit, and Coulomb interactions simultaneously. However, such a calculation could lead to some rather interesting results, particularly for Ir^{4+}, which has a very large ζ and should have a rather large splitting of the ^6S ground state.

TABLE 17. DATA ON IONS WITH nd^5 CONFIGURATION[a]

Ion	Configuration	$\langle r^2 \rangle$ ($Å^2$)	$\langle r^4 \rangle$ ($Å^4$)	i.r.[b] (Å)	Δ (cm^{-1})
Mn^{2+}	$3d^5$	0.4277	0.4145	0.830	26,846[c]
Fe^{3+}	$3d^5$	0.3196	0.2168	0.49[d]	~32,000[e]
Ru^{3+}	$4d^5$	0.6479	0.7175	0.68	---
Rh^{4+}	$4d^5$	---	---	0.615	---
Ir^{4+}	$5d^5$	---	---	0.63	---

[a]*Values of $\langle r^n \rangle$ and ionic radius are from references 17 and 16, respectively. The quantity Δ is the difference in energy between ^4G and ^6S states in the free ion.*

[b]*i.r. = ionic radius.*

[c]*C. Corliss and J. Sugar, Energy Levels of Manganese, MnI through MnXXV, J. Phys. Chem. Ref. Data 6 (1977), 1253.*

[d]*For 4-coordination.*

[e]*C. Corliss and J. Sugar, Energy Levels of Iron, FeI through FeXXVI, J. Phys. Chem. Ref. Data 11 (1982), 135.*

TABLE 18. CRYSTAL-FIELD PARAMETERS, B_{nm} (cm^{-1}), FOR nd^5 IONS IN Ga^{3+} SITE IN GSGG

Ion	B_{20}	B_{40}	B_{44}	B_{40}^c
Mn^{2+}	316.1	-5,699	2,286	-5,004
Fe^{3+}	236.2	-2,981	1,196	-2,618
Ru^{3+}	478.8	-9,865	3,957	-8,663

9. CONCLUSION AND SUGGESTIONS FOR FURTHER WORK

In our discussion of the crystal-field splittings of the Hund ground state of the nd^N configurations, particular ions were singled out for further work. Because of the lack of experimental data on ions in the particular host, $Gd_3Sc_2Ga_3O_{12}$, chosen for our investigation, either experimental work should be performed or we might shift our attention to different hosts where experimental data are available. If different hosts are considered, we would suggest attention towards fluorides rather than oxides, as it has been our experience in the study of rare-earth spectra* that for the fluorides the point-charge model of crystal fields agrees well with experiment. In the oxides, the point-charge model has had mixed success.*

**The theory for rare-earth ions is discussed in a sequence of 14 technical reports of Harry Diamond Laboratories published between October 1973 and February 1977, entitled Rare Earth Ion-Host Interactions.*

In a number of cases it was pointed out that the next higher level must be taken into account (e.g., Ti^{2+} in sect. 5), since the predicted crystal-field splitting is of the same order as the free-ion separation of the levels (in Ti^{3+} the ^3F-^3P spacing). In these cases the Coulomb interaction described by the Slater parameters $F^{(k)}$ must be considered; these, generally, are obtained from the free-ion data where available.* The dependence of the $F^{(k)}$ on a particular host crystal can be approximated by the theory developed elsewhere.[19]

For the nd^N ions in ionization states greater than 3, no values of $\langle r^n \rangle$ are available.[17] Perhaps a method employing simple Slater orbitals, which have been used successfully in rare-earth ions,† can be used to obtain usable estimates of $\langle r^n \rangle$. Recently, a more sophisticated approach to Slater orbitals has been published[20] which may be applied to obrain more accurate values of $\langle r^k \rangle$.

The effect of including the spin-orbit interaction should be investigated more thoroughly, particularly for the ions in the nd^N series for $N > 5$. In general for $N > 5$, the spin-orbit constant becomes quite large, and the weak-field approximation should be augmented to include this interaction. That is, we assume that the crystal-field and spin-orbit interactions are approximately equal but both much less than the Coulomb interaction. Such an approximation is valid in the configurations with $N > 5$.

As we mentioned earlier, the point-charge model of crystal fields is very reliable for the fluoride host materials. Professor D. Gabbe of the Massachusetts Institute of Technology has made us aware of a number of fluoride garnets‡ which have the same crystal structures as GSGG. These fluoride garnets are of the form $Na_3M_2Li_3F_{12}$, with M = Sc, In, or Rh and where

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[17] *S. Fraga, J. Karwowski, and K. M. S. Saxena, Physical Sciences Data, Vol. 5, Handbook of Atomic Data, Elsevier/North-Holland, New York (1976). [The values of $\langle r^k \rangle$ are not reported for ionization states greater than 3.]*

[19] *C. A. Morrison, Host Dependence of the Rare-Earth Ion Energy Separation $4f^N$-$4f^{N-1}$ $n\ell$, J. Chem. Phys. 72 (1980), 1001.*

[20] *V. Maráz, Approximate Functions for 4s, 4p Slater-Orbitals for Transition Metal Ions having d^N Electron Configurations, Acta Phys. Chem. 23 (1977), 225.*

**J. Sugar, private communication. Much of the work reported by C. E. Moore (Atomic Energy Levels as Derived from the Analysis of Optical Spectra, volumes I, II, and III, National Bureau of Standards, 1971) is being updated and reported in J. Phys. Chem. Ref. Data.*

†R. P. Leavitt and C. A. Morrison, Simple Model for the Energy Gap and its Variation with Pressure in Rare-Earth Monochalcogenides, Phys. Rev. B (manuscript in preparation).

‡We wish to thank Professor D. Gabbe of MIT for copies of a number of papers on fluorinated host materials, including J. Sugar and C. Corliss, Energy Levels of Vanadium, VI through VXXIII, J. Phys. Chem. Ref. Data 7 (1978), 1191.

the M site has C_{3i} symmetry.[21] It would be possible to dope a large number of nd^N ions into the M site (16(a) site in space group No. 230, with C_{3i} symmetry). The calculation of the crystal-field splitting in C_{3i} symmetry is partially complete and should not present a great deal of difficulty.

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[21]*R. de Pape, J. Portier, J. Grannec, G. Gauthier, and P. Hagemuller, Sur quelques nouveaux grenats fluorés, C. R. Acad. Sc. Paris* *__269__*, *serie C (1969), 1120.*

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